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THESIS

PHASE EQUILIBRIUM IN POLY-COMPONENT GAS-LIQUID HYDROCARBON SYSTEMS

EXPERIMENTS ON SELECTED WHOLE TURNER VALLEY MIXTURES:

by

L.A. McLeod, B. Sc.

University of Alberta,
Edmonton, Alberta.

September, 1942

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A THESIS

PHASE EQUILIBRIA IN POLY-COMPONENT GAS-LIQUID HYDROCARBON SYSTEMS

The pressure-volume-temperature relations in a natural gas over the temperature range, 25° to 77°C., and the pressure range, 0 to 190 atm.

and

a study of the equilibrium behavior of the gas-liquid system, composed of the whole product of a Turner Valley oil well.

University of Alberta,
Department of Chemistry,
September, 1942

By - L.A. McLeod, B.Sc.
Under the direction of -
Dr. E.H. Boomer.

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PHASE EQUILIBRIA IN POLY-COMPONENT GAS-LIQUID HYDROCARBON SYSTEMS

Submitted in Partial Fulfilment
of the
Requirements for the Degree of
Master of Science

by

Lloyd Alexander McLeod, B. Sc.

Under the Direction of
Dr. E. H. Boomer

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INTRODUCTION

During the past fifty years much attention has been paid to the physical equilibrium existing between gas and liquid phases. Preliminary investigations involved relatively simple two component systems but as the need for knowledge of the behavior of more complex systems became apparent in the field of industry, the investigations were extended to include more complex systems such as are discussed in this thesis.

The present work is concerned with a relatively important section of the field of phase equilibrium studies -- viz the equilibrium between two phase, gas-liquid hydrocarbon systems. The importance of this work arises from the necessity for knowledge of pressure-volume-temperature-composition relations as applied to the petroleum industry. Until quite recently accurate calculations involved in oil well production and petroleum refining were limited to regions of relatively low pressure and temperature -- i.e. regions in which the ideal laws of Henry and Raoult were relatively accurate. Recent advances in petroleum technology have necessitated a knowledge of the behavior of naturally-occurring hydrocarbon systems under conditions of temperature and pressure far beyond the region in which these ideal laws are applicable.

Comprehensive studies of phase equilibria over wide ranges of temperature and pressure in two phase systems

of this type may be considered to have started about 1930. Early studies involved commonly only two component systems and investigations of complex naturally-occurring systems are limited very largely to the past three or four years. The increasing interest in this field is evidenced by the increasing number of articles appearing in current literature.

The purpose of such investigations is primarily to provide the necessary data for accurate calculations concerning the behaviour of naturally-occurring systems in the production and processing of petroleum. Theoretical interest also pertains to these studies in so far as data are provided for evaluation of coefficients in empirical and theoretical equations of state and for confirmation of the kinetic-molecular theory and theories pertaining to intermolecular forces. These data are available from the pressure-volume-temperature relationships of the gaseous state, determination of which is a necessary preliminary procedure to two phase equilibrium studies.

The purpose of the current work is of a two-fold nature. First, it is hoped that the information derived herein, will be of value in the proper operation and exploitation of the crude oil field existing in Turner Valley. At the present time investigations are being pursued (2) in the development of a new plan of operation of wells in the Turner Valley field based on removal from each well of the oil and gas content of a

certain maximum volume of reservoir space per unit area per unit time. Proper application of this plan depends almost entirely on an accurate knowledge of the phase densities of the two phases in the producing horizon. It is hoped that the present work will provide information necessary for the calculation of these phase densities and also of the effect on these densities of decreasing reservoir pressure with time.

Second, the validity of certain suggested equations of state may be subjected to confirmation, or suitable new expressions may be derived. The derived data will serve to increase the already large fund of information concerning fugacities and thermodynamic properties of gaseous hydrocarbon mixtures.

This work is a continuation of a series of investigations grouped under the general heading "Phase Equilibria in Hydrocarbon Systems". The project has been under investigation in these laboratories since 1931, at which time the studies were limited to simple two-component systems. Although such studies could have been continued almost without limit, it was found desirable to extend the scope of the work to include complex polycomponent systems more nearly related to those found in practice.

Studies on complex naturally-occurring systems were initiated by Gillies and Hugill (6) on a natural gas-naphtha sample from a well located in the Turner Valley gas cap area. Upon discovery of a crude oil zone in the

Turner Valley field it was felt necessary to extend the work to a system consisting of crude oil-natural gas. Preliminary studies on a system of this type using Turner Valley limestone zone crude oil and Viking natural gas were begun by Davis and Boyer (4) and continued by Boyer and Morrison (1) on a system of Turner Valley natural gas and crude oil, both from the same well. Sufficient information was obtained to establish the method used and the accuracy of the analytical system involved. In addition to the equilibrium measurements reported by these authors (1,6), pressure-volume-temperature measurements on natural gas, and application of Lewis' fugacity rule to hydrocarbon mixtures have been reported.

The present work is a direct continuation of the work of Boyer and Morrison with a view to investigating the effect on the two phase gas-liquid equilibrium, of variation in pressure, temperature, and gas:oil ratio. In addition, the pressure-volume-temperature relations of the natural gas have been determined as a necessary preliminary step to the main investigation. The variation of the fugacity of the gas with pressure has been determined graphically and comparison made to that calculated using Lewis' fugacity rule.

LITERATURE

In recent years the number of papers pertaining to phase equilibria in hydrocarbon systems has become increasingly large. Comprehensive reviews of the literature concerning solubilities in simple systems appear in theses by Johnson (8) and Piercey (17). Gillies and Hugill (6) extended this bibliography to papers concerning more complex hydrocarbon systems. Boyer and Morrison (1) reviewed the literature pertaining to pressure-volume-temperature measurements and also equilibrium studies of recent date. It is the intention in this review to refer only to those papers of particular significance in the present work and to those papers published during the past year.

Mention might be made of the work of Jessen and Lightfoot (7) on pressure-volume-temperature data for n-butane, n-pentane mixtures and for the pure substances at 30°C. Since the method used, involved expansion of a known volume of gas into a larger volume and measurement of the resultant pressure, it is felt that these data are not as reliable as those of Sage et al referred to by Boyer (1).

Nielsen (15) has discussed the phenomenon of retrograde condensation from the kinetic molecular viewpoint. As pressure is increased, the Van der Waals forces of the light molecules in the gas phase become relatively more important than similar forces tending to hold the heavier molecules in the liquid phase. These forces between

heavier molecules in the liquid phase are also weakened by solution of light molecules in the liquid phase. The result is transfer of heavy molecules to the gas phase with increasing pressure.

Reference has already been made (1) to the work of Kay on equilibrium studies in the systems ethane-normal heptane and ethane-normal butane. This work has been continued (11) to include the normal butane-normal heptane system. By comparison of equilibrium constants for butane in ethane and heptane and for heptane in ethane and butane the author concludes that the critical temperature of any binary system involving two of these components is closely proportional to the sum of the products of weight fractions and critical temperatures of the pure constituents. In all three binary systems, the critical pressure-composition graph shows a maximum which is related to the absolute molecular weight and the difference in molecular weights of the constituents. The first members of the paraffin series exert a greater effect than do higher members.

Sage, Lacey et al (3, 16, 20, 22) have continued their extensive studies on two-component hydrocarbon systems, and subsequent calculation of thermodynamic properties of these systems. Sage and Lacey (19) have attempted to correlate equilibrium constants for methane in a variety of hydrocarbon systems with temperature, pressure, molecular weight and chemical nature of the components other than methane. No account has been taken

of the variation in the ratio of methane to less volatile constituent. The results are, at best, qualitative but provide a good correlation of existing data in a variety of systems. The authors advise against unrestricted application of these correlations to systems not strictly paraffinic in nature.

Sage, Hicks and Lacey (21) provide a correlation of data on equilibrium constants for lighter paraffins from methane to heptane in naturally-occurring systems. The treatment of methane and ethane and a less volatile constituent is fairly detailed and the results are considered reliable. Data for all other hydrocarbons considered, were supplied almost entirely from the work of Katz (9) and based on the behavior of ideal solutions in low pressure regions. Due to lack of available data the paper does not discuss the effect of variation in relative amounts of the different constituents. Discussion of the effect of constituents lighter than pentane on the equilibrium constants for lighter hydrocarbons is omitted also.

Shiah (23) has made use of a simple integration of the Clapeyron equation to correlate all existing plots of equilibrium constants vs temperature and pressure. He shows that a plot of the natural logarithm of the equilibrium constant vs the reciprocal of the absolute temperature is, for practical purposes, a straight line for systems on which data are available. On plotting reciprocals of temperature for different substances against

the reciprocal of the temperature at which a reference substance has the same equilibrium constant, a straight line is obtained. To determine the equilibrium constant at any temperature for any hydrocarbon, one needs only to find from this plot, the temperature at which the reference hydrocarbon (pentane for convenience) has the same equilibrium constant. From a plot of equilibrium constant vs temperature for the reference hydrocarbon (pentane), the value of the equilibrium constant may be determined. The graph may be adapted for use in complex systems where the average molecular weight of the hydrocarbons is known.

Dodge and Newton (5) develop a differential equation relating pressure and composition of both liquid and vapor phases in equilibrium at constant temperature. Identical developments are made using free energy and fugacity. The equation may be integrated on the assumption of ideal conditions, and applications to specific cases are shown.

THEORETICAL

Original considerations of two phase gas-liquid systems at equilibrium were based on the ideal laws of Raoult and Henry. Both these laws assume ideal liquids and gases, i.e. the change in the free energy (ΔF) is proportional to the logarithm of the molar concentrations, and the vapor pressure is independent of the total pressure on the liquid. At low pressures they apply reasonably well to hydrocarbon systems.

That liquid and gaseous solutions are not ideal has been long known and many devices such as activity and fugacity have been developed as a result (12).

That vapor pressure is a function of total pressure on a liquid, was shown by Poynting (18). He showed from thermodynamical considerations that -

$$\left(\frac{dP_1}{dP_2}\right)_{T,X} = \left(\frac{\bar{V}_2}{\bar{V}_1}\right)_{T,X}$$

Where P_1 = vapor pressure of liquid
P_2 = total pressure on liquid
$\bar{V}_2$ = partial molal volume of liquid
$\bar{V}_1$ = partial molal volume of vapor

In words, the increase in vapor pressure of a liquid with increase in total pressure on the liquid, is proportional to the partial molal volumes of liquid and vapor. The equation may be integrated easily, assuming that no solution of gas in liquid occurs with increasing pressure. Such an assumption makes the integration invalid as far as naturally-occurring hydrocarbon systems are concerned.

For application to the present case, it is necessary

to have an equation for each phase relating composition and pressure. Johnson (8) develops differential equations of this type for two-component systems but, before integration can be carried out, it is necessary to have an equation of state for each phase. Such equations of state are not readily available at the present time. Johnson concludes that it is easier to measure experimentally the properties of the individual phases and set up empirical rules than to evaluate the coefficients of an equation of state for each phase. In the present studies on poly-component systems, this conclusion appears even more applicable.

In representing a two-component gas-liquid system, the customary practice is to make use of Gibb's Phase Rule $F = C - P + 2$. By restricting one of the variables, a univariant system is obtained which is readily represented graphically. However similar representation of a polycomponent system, as in the present case, is more difficult. In view of the difficulties entailed in developing a suitable equation of state for each phase, it has become customary to represent equilibrium conditions by the so-called "equilibrium constants". The constant is defined as -

$$K = \left(\frac{C_1^G}{C_1^L}\right)_T$$

where C_1^G = mole fraction of component 1 in the gas phase.
C_1^L = mole fraction of component 1 in the liquid phase.

A true constant would be expected if both phases behaved ideally. Since this is not the case, a variation in K

with pressure at constant temperature is not unexpected. Only by replacing concentrations by activities or fugacities, can a constant ratio be expected. The constant K, as defined, would be expected to follow the general trend of the constants reported by Katz and Hackmuth (9) and other similar investigations. In the case of complex hydrocarbon systems, it may be predicted that K for methane would decrease regularly with increasing pressure, due to solubility of methane in the oil, and vaporization of the oil, until a value of 1 is reached at the critical pressure where the system becomes single phase. Constants of less volatile components should show an initial decrease, followed by an increase to 1, due to transfer of less-volatile components to the gas phase. The physical result of this effect of Poynting's rule gives rise to the so-called "region of retrograde condensation".

Attention is drawn to the discussion by Katz and Kurata (10) on the proper application of the term "retrograde condensation". In this region, at constant temperature, an increase in pressure results in an increased volatilization of liquid into the gas phase. It is in this region that the equilibrium constants, K, for the liquid components, having passed through a minimum value, are increasing with increasing pressure.

The variation of phase densities with pressure is as would be predicted. The liquid phase density shows a continued decrease with increasing pressure due to solubility of lighter components from the gas phase and transfer of

heavier components to the gas phase. The gas phase density shows a continued increase due to the normal effect of compression of the gas, transfer of heavier components from the liquid phase and preferential solution of lighter components in the liquid phase. At the critical pressure, the phase densities become identical.

While it is always found, and may be predicted, that the solubility of gas in liquid increases with pressure on the system, the behavior with respect to changing temperature is not so simple. For ideal, simple systems, solubility of gas in liquid, decreases with increasing temperature. For a real system, this is not necessarily true and, in fact, the phenomenon of increasing solubility with increasing temperature might be expected in regions of high pressure and temperature. The result of this effect on phase densities is a rather rapid decrease in liquid phase density with increasing temperature. Given the correct conditions, a simultaneous increase in gas phase density, due to rapidly increasing volatility of heavier components, may occur.

The effect is common and has been demonstrated in these laboratories by Johnson (8). It is associated with relatively greater transfer of the normally liquid components, as compared to transfer of gas components, to the gas phase. The effect of increasing temperature on the position of the region of retrograde condensation is to reduce the pressure at which the phenomenon occurs.

Although very little information is available on the

effect of variation in the gas/oil ratio on the system at equilibrium, it seems reasonable to predict that an increased gas/oil ratio would tend to decrease the gas phase density due to dilution of the heavier components with lighter; simultaneously the liquid phase density might be expected to increase due to more complete transfer of more volatile components to the gas phase.

As has been mentioned before, the determination of pressure-volume-temperature data on the natural gas sample is a necessary preliminary step to the equilibrium studies. These data can be expressed in the form of empirical or theoretical equations of state, several of which have been proposed elsewhere. Any such equation of state is limited in its application to the relatively narrow limits over which its coefficients are valid. A convenient representation of pressure-volume-temperature data lies in the fugacity (12). Fugacities were determined on the Turner Valley natural gas sample used in this investigation, by evaluation of the expression -

$$RT \ln \frac{f}{P} = -\int_0^P a\,dP$$

Where f = fugacity
a = residual volume
$= \frac{RT}{P} - V$
and P, V, T, R, have their usual significance.

The residual volume, a, is defined as the difference between the actual volume of the gas at pressure P, and the volume that would be occupied by the gas if ideal. The equation is developed from the fundamental equation -

$$\frac{dF}{dP} = V$$

Substitution for V by the ideal gas law leads to the simple result

$$dF = RT\ d\ \ln P.$$

For a real gas, Lewis (12) suggested the use of the quantity "fugacity", f, in place of P to avoid the use of a complex equation of state. Thus -

$$dF = RT\ d\ \ln f.$$

$$\text{Or}\quad \Delta F = RT \ln \frac{f_1}{f_2}$$

As P ⟶ 0, the gas behaves more ideally and hence

$$f \longrightarrow P \quad \text{as } P \longrightarrow 0$$

Combining this with the above expression, $\frac{dF}{dP} = V$

we get

$$RT\ d\ \ln f = V\ dP$$

$$\text{Then } RT \ln \frac{f_1}{f_2} = \int_{P_1}^{P_2} V\ dP$$

Substituting $\frac{RT}{P} - a$ for V, we get

$$RT \ln \frac{f_1}{f_2} = \int_{P_1}^{P_2} \frac{RT}{P}\ dP - \int_{P_1}^{P_2} a dP$$

$$\text{Or}\quad RT \ln f = RT \ln P - \int_0^P a dP$$

since f ⟶ P as P ⟶ 0

$$\text{Thus}\quad RT \ln \frac{f}{P} = -\int_0^P a dP.$$

The integral was evaluated graphically from a plot of a vs P and hence values of f were obtained.

At low pressures, it is possible to calculate with reasonable precision the partial gas pressures in a gas mixture of known composition and total pressure by Dalton's law. However in regions of higher pressures, Dalton's law fails to apply and recourse must be had to

other means. Lewis (12) has proposed a useful rule of the form:

$$f_1 = N_1 f_1^{\circ} \text{ and}$$

$$f_t = f_1^{\circ} N_1 + f_2^{\circ} N_2 + \text{-----}$$

Where f_1 = fugacity of component 1 in a gaseous mixture.

N_1 = mole fraction of component 1 in a gaseous mixture.

f_1° = fugacity of pure component 1 at the same temperature and pressure

f_t = fugacity of the mixture.

Verification of this rule would make it possible to calculate the fugacity of a gaseous mixture from its composition, knowing the fugacities of the pure components. The fugacities of many pure substances are fairly accurately established.

MATERIALS

The samples of natural gas and crude oil used in these experiments were obtained from the North West Hudson's Bay #6 well in Turner Valley. This well was the farthest south producing well in the Turner Valley field and is located in LSD 7, Section 8, Township 18, Range 2, West of the 5th Meridian. This well was completed on September 20, 1941 at a total depth of 8235'. Only the upper porous zone (7870' - 7970') was encountered. In February, 1942, when the samples were taken the well was producing at the rate of 500 barrels per day with a gas/oil ratio of 1500 cu.ft. per barrel. The bottom-hole pressure as determined on October 19, 1941, was 2577 psi and the bottom-hole temperature was 170°F.

The gas sample was taken through a ½" valve on the 3" fuel line from the separator. The oil sample was taken through the bottom valve on the oil level gauge on the separator. Eight standard gas cylinders and three small pressure cylinders were used to collect the gas sample and a fourth small cylinder was used to collect the oil sample. The oil container was first filled with water which was then slowly displaced by oil from the separator. The oil sample was taken continuously at the separator pressure at such a rate that the cylinder was completely filled just as the last gas cylinder was filled. The gas cylinders were flushed three times by building up the pressure in them to 200 psi and then blowing off to atmosphere. Gas samples were taken every half hour. During the period of sampling, the well was

produced at a steady rate. Sampling was done by the field staff of the Petroleum and Natural Gas Conservation Board, supervised by Harrison H. Heisler.

On receipt of the samples, they were purified in a similar manner to that described by Boyer(1). The gas sample was scrubbed to remove hydrogen sulfide and mercaptans by bubbling through 40% KOH in a glass column packed with short lengths of glass tubing. The clean gas was stored in a gas holder from which it was compressed through a Calcium chloride drier into the low pressure storage system. The gas liberated from solution in the oil was added to that from the gas cylinders and the whole gas sample was mixed until a constant analysis was obtained.

After the gas in solution in the oil had been liberated, the oil was displaced by water and, after being scrubbed in the same caustic column, was collected and stored over water.

The gas composition was determined in a low temperature fractional distillation apparatus (6). An average of four analyses on the original gas gave a composition of:

Component	Volume %
Methane	78.93
Ethane	10.90
Propane	4.85
Butane	2.19
Pentanes +	0.60
Nitrogen	2.53

The density of the gas was determined by weighing a calibrated bulb containing the gas at known temperature and pressure. The average of 18 densities was 8.151×10^{-4}g/cc. at 25°C and 76 cm. The average deviation from this value

was 1.5 parts per 1000.

Density of the crude oil was determined by weighing a known volume of oil at 20°C and 25°C.

$$d^{20^\circ}_{4^\circ} = 0.8151 \text{ g/cc.}$$

$$d^{25^\circ}_{4^\circ} = 0.8111 \text{ g/cc.}$$

The mean Molecular weight of the crude oil was determined by the cryoscopic method (6,17) and found to be 174.5 g.

The crude oil was fractionally distilled and refractive indices of successive fractions plotted against their densities and mean molecular weights. The results are shown in Table 1 and plotted in Figure 1.

Table 1.

Molecular weight - refractive index - density measurements on crude oil fractions.

% over	Molecular weight	Refractive index	Density
5		1.3862	0.6724
6	83.0	1.3784	
9	85.4	1.3848	
10		1.3900	0.6867
12	88.8	1.3909	
12.6	101.9	1.3902	
14	80.	1.3959	
15		1.3941	0.6929
15	93.8	1.3954	
16.8	91.9	1.3966	
18	91.7	1.4008	
19.2	97	1.3999	
20		1.3981	0.7050
20.2	98.3	1.4021	
21	100.6	1.4024	
21.6	96.1	1.4038	
23	100.6	1.4060	
23	101.0	1.4074	

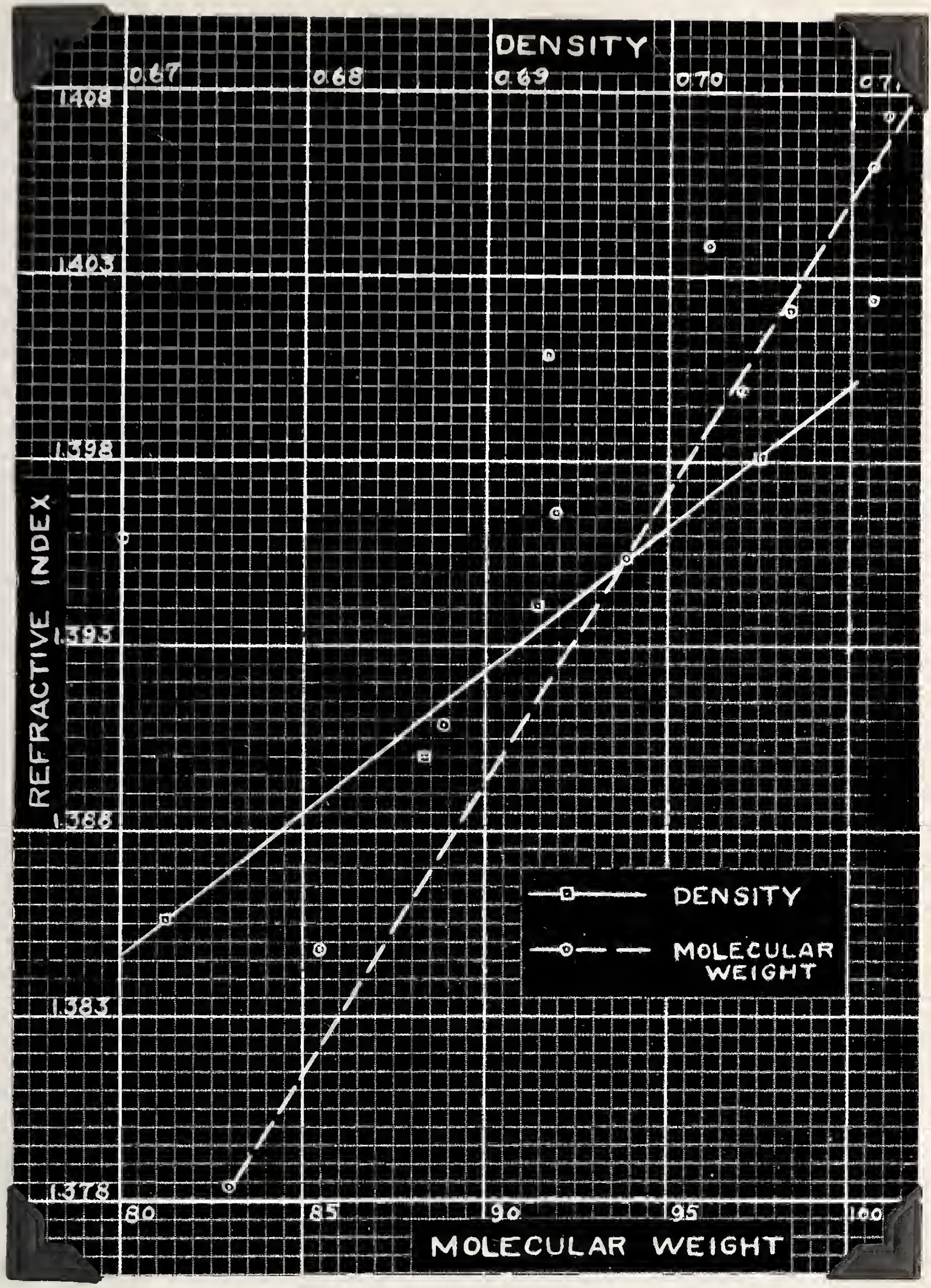

Figure 1

Variation of Refractive Index

with Density and Molecular Weight

APPARATUS

The experimental apparatus is identical with that described in detail by Boyer (1). It consists of three main parts:

1. High pressure storage systems and equilibrium cylinder.
2. Low pressure analytical system.
3. Crude oil storage and dispensing system.

The high pressure system consists essentially of a drier, a gas measuring pipette, a deadweight piston gauge and the equilibrium cylinder and pipettes. Gas from the storage tanks is admitted to the high pressure systems by means of a compressor and passes through a KOH drier surrounded by an air bath at 60°C, into the measuring pipette which is kept at 60°C ± 0.15° by means of a thermostatically controlled oil bath. The approximate pressure in the pipette or in the drier can be read on a Bourdon gauge. The pipette can be connected to the deadweight piston gauge and to the equilibrium cylinder. To prevent solution of the gas in the castor oil of the piston gauge, a mercury U tube is inserted in the line. Level of the mercury in the U is shown by deflection of a galvanometer needle placed in a circuit which terminates in a platinum point at the mercury surface and in the wall of the U tube. Pressure in the pipette may be increased by a hydraulic mercury pump.

The equilibrium cylinder, a complete description of which is given by Boyer (1) is totally immersed in a thermostatically controlled oil bath heated by two 1500

watt heaters, one of which is connected to a relay circuit. The cylinder may be raised from the bath for charging and for taking equilibrium samples.

To prevent possible condensation of higher hydrocarbons under high pressure, all high pressure lines, including the compressor, drier and U tube, are maintained at 60°C by suitable heaters.

The equilibrium cylinder consists essentially of a hollow steel cylinder 3 1/16" I.D. Copper connections join the cylinder to gas and liquid sample pipettes which may be shut off by valves located at each end of the pipettes. A pump assembly, driven by a drive shaft passing through one end of the cylinder, circulates gas through the gas sample pipette, which is located in a vertical position above the cylinder, and, simultaneously, liquid through the liquid sample pipette which is located in a vertical position below the cylinder. For this series of experiments, a steel half cylinder 5" long and 2 15/16" in diameter was fitted into the equilibrium cylinder between the pumps and the opposite end plate. This plug reduced the volume of materials needed for an experiment and permitted the use of much lower gas/oil ratios than would otherwise have been the case.

The analytical system is unchanged from that described by Boyer (1). It consists essentially of a condenser train, a gas storage and measuring system, and the low temperature fractional distillation column. The apparatus can be completely evacuated by means of a

two-stage mercury diffusion pump backed by a Hyvac oil pump. The sample pipettes can be connected to a standard steel connector. The first condenser is removable and is connected to the apparatus by a ground glass joint. The second condenser is surrounded by a mixture of dry ice and acetone and the third condenser is cooled by dry ice-acetone under vacuum. These mixtures maintain the condensers at -79°C and -112°C respectively, which temperatures are read by means of double junction copper-constantan thermocouples. A small graduated tube of about 5 cc. capacity is joined to the condenser train by means of a thin-walled capillary. This tube is for trapping the liquid retained in the condensers when the gas phase sample is expanded. The liquid is distilled into this tube at the temperature of liquid air and the capillary is sealed with an oxygen-gas flame. A third condenser in the train can be surrounded by liquid air at the proper time.

The condenser train is connected to the gas measuring system by means of a manually operated Toepler pump. The measuring system consists of six 1 litre flasks inside an air bath. Any or all of these flasks can be connected to the Toepler pump and to a constant volume manometer.

The low temperature fractionation column is unchanged from that described by Gillies and Hugill (6).

The crude oil is dispensed from the carboy in which it is stored over water by displacement with water from a reservoir. It is dried over Calcium chloride and measured

into a one litre flask. After weighing, it can be dispensed into the equilibrium cylinder through a capillary tube equipped with a ground glass joint to fit a standard taper male connection on the cylinder. All glass connections are lubricated by a gel of mannitol and glycerol in which the oil is insoluble.

PROCEDURE

Pressure-volume-temperature relationships

The gas sample pipette, evacuated and suspended in the oil bath at the proper temperature, was filled to the desired pressure by means of the compressor and the hydraulic mercury pump. Fine adjustment of the pressure was made on the deadweight gauge and then the valve on the pipette was closed. The other end of the pipette was connected by a high pressure line to the glass analytical system. With all necessary parts of the apparatus evacuated, the gas sample was expanded into the analytical system and transferred into the bulbs by means of the Toepler pump until a residual pressure of less than 1 mm. of mercury could be read by means of a McLeod gauge. The temperature of the bulbs was brought to a constant value by forced circulation of air and the pressure in the bulbs measured on the manometer. Density measurements were made on this gas. Calculation of the pressure-volume-temperature data was according to the following procedure:

The pressure-volume product, PV, of the compressed gas at temperature T is represented by

$$(PV) = \frac{(P_{DW} + P_A)\, V_{GP}}{14.696} \quad \text{cc. atmos.}$$

Where P_{DW} = Pressure reading on deadweight gauge in psi.

P_A = Atmospheric pressure in psi.

V_{GP} = Volume of gas pipette in cc.

The pressure-volume product, $(P_1V_1)^1$, of the expanded gas at 25°C and 76 cm. of mercury is expressed by -

$$(P_1V_1)^1 = \frac{P_m}{76}\left[V_s + \frac{(V_r + V_{GP})\,P_{McL}}{P_m}\right]\frac{298.1}{T} \text{ cc. atmos.}$$

Where $(P_1V_1)^1$ = PV product using the ideal gas laws to correct to 25° and 76 cm.

P_m = pressure of manometer in cm. of mercury at 0°C.

V_s = volume of storage system in cc.

V_r = volume of condenser train in cc.

V_{GP} = volume of gas pipette in cc.

P_{McL} = residual pressure on McLeod gauge in cm. of mercury.

T = absolute temperature of storage system.

This value of $(P_1V_1)^1$ must now be corrected for deviation of the gas from ideality at 1 atmosphere.

$$\frac{(P_1V_1)}{(P_1V_1)^1} = 1 - \lambda$$

$$= 1 - b\,\Delta P$$

Where (P_1V_1) = corrected PV product at 25°C and 76 cm. of mercury.

λ = deviation factor for the gas at 1 atmosphere.

b = deviation factor per cm.

ΔP = $76 - P_m$

$\frac{(PV)}{(P_1V_1)}$ is then plotted against P (Figure 2)

Equilibrium Measurements

The equilibrium cylinder, previously tested for leaks, was set in place in the oil bath and valves on both pipettes opened. The capillary connection, used for charging the oil, was put in place and the cylinder was completely evacuated.

A sample of oil was drawn from the oil storage and chilled in ice. After weighing the flask and the oil, the latter was charged into the cylinder through the capillary glass connection by allowing atmospheric pressure to force the oil into the evacuated cylinder. When nearly all the oil had been charged, the vacuum remaining in the cylinder was noted on a manometer attached to the capillary glass connection and then natural gas was admitted to bring the pressure up to atmospheric. The liquid sampler was removed and the standard steel male connection on the cylinder was quickly closed by screwing in a plug. The weight of the empty flask determined the weight of oil charged.

The volume of gas at 25°C and 76 cm. of mercury to give a desired gas/oil ratio, was then calculated and converted, using the PV/P_1V_1 - P curve, to volume at 60°C and 1500 psi. All mercury was drained from the gas measuring pipette and the gas pressure therein was raised to exactly 1500 psi at 60°C as measured on the deadweight gauge. This gas was charged into the cylinder and the pressure in the pipette restored to exactly 1500 psi at 60°C by draining off mercury. The actual volume of gas added at 1500 psi and 60°C was found by weighing the mercury used to displace it from the pipette. This procedure was repeated until the desired gas/oil ratio in the cylinder was attained. The equilibrium cylinder was then connected directly to the deadweight gauge and the circulating pumps started. When a constant pressure had

been reached in the cylinder, a condition of equilibrium was assumed to exist and the pumps were shut off. Equilibrium was usually attained within an hour of adding the final charge of gas, particularly if the pumps had been operating during the gas charging operations. The cylinder was rapidly raised from the bath and both pipettes closed off at once. Pressure was released from the cylinder and the pipettes disconnected.

Expansion of Gas Phase Sample.

With the glass apparatus evacuated and the proper temperatures in the dry ice-acetone mixtures around the condensers, the phase sample was expanded slowly into the bulbs. The uncondensed gas was transferred to the bulbs to a residual pressure of 0.1 mm. of mercury and then the third condenser was surrounded by liquid air. This completely removed butanes and lighter from the condenser train, with a minimum of pentanes. The condensate from the liquid air trap was added to the gas in the bulbs and, after constant temperature had been attained, the pressure was read on the constant-volume manometer. The gas was then circulated automatically (13) until it was thoroughly mixed. Six hours was considered sufficient. Duplicate density measurements were made and samples taken for low temperature analyses.

The liquid separated in the dry ice-acetone condensers was distilled over into the graduated dilatometer using liquid air, and the dilatometer was sealed off. Its weight was determined and the volume and refractive index of liquid at 20°C measured.

Expansion of Liquid Phase Sample

This was carried out in identical fashion to the above. To prevent violent ebullition of gas from solution in the oil at very low pressures, the oil was stirred by a magnetic stirrer operated manually by a solenoid. When the last of the butanes and lighter components had been removed to the bulbs, the condensers were lowered and a dry ice-acetone mixture placed in the cup which was soldered to the pipette. Thus liquid was distilled into the pipette and it was thereby washed of any oily residue. This procedure was repeated three or four times. Liquid air was then placed around the oil condenser and all fractions distilled into it. The condenser was removed and fitted with a ground glass cap. The weight of oil, its density at 20°C, and mean molecular weight were determined. An A.S.T.M. distillation was done on the oil and refractive indices determined for successive fractions using an Abbé refractometer.

RESULTS AND DISCUSSION

The results are presented in two distinct sections:

1. Pressure-volume-temperature relationships of natural gas from N.W. Hudson's Bay #6, and comparison with other gases of a similar nature.
2. Two phase gas-liquid equilibrium measurements on the natural gas-crude oil system.

Pressure-Volume-Temperature Relationships

A complete series of PV vs P values was determined for this gas, at 60°C in the pressure range 1 - 190 atmospheres. One point was determined at 25°C and two points at 77°C. The experimental results are presented in Table 2. Smoothed values at 60°C obtained from a large-scale plot are presented in Table 3.

All values listed in Table 3 are for $(PV)_{P,T}/(P_1V_1)_{25^\circ}$. To convert these ratios into specific values of PV/g of gas it is necessary to know either the density or the molecular weight of the gas for a particular condition. Both of these methods were used.

The average of 18 densities at approximately 60 cm. of mercury and 25°C was 6.435×10^{-4}g/cc. The average deviation was 0.15%. This gives a value for $(PV)_{25^\circ, 60 \text{ cm.}}$ of 1226.84 cc,atm./g. This value could be used to calculate the molecular weight of the gas but inaccuracy due to deviation of the gas from ideality must first be corrected.

Table 2.

Experimental values of $PV/(P_1V_1)$ as a function of Pressure at 25°C, 60°C, and 77°C for N.W. Hudson's Bay #6 Natural Gas.

P. Atm.	25°C	60°C	77°C
17.94		1.0779	
		1.0787	
34.95		1.0441	
		1.0444	
51.95		1.0137	
		1.0129	
		1.0108	
		1.0105	
68.97		0.9736	
		0.9737	
85.98		0.9507	
		0.9505	
102.99	0.7274	0.9299	1.0147
	0.7304	0.9303	1.0129
120.01		0.9142	
		0.9146	
137.02		0.9020	
		0.9026	
154.03		0.8977	
		0.8979	
171.04		0.8977	0.9842
		0.8985	0.9832
188.06		0.9048	
		0.9050	

Table 3.

Smoothed Values of $PV/(P_1V_1)$ from Curves through Experimental Points at 60°C.

P. atm.	N.W.H.B.#6	A.O.I. #2	Royalite 27
0	1.1205	1.1211	1.1204
20	1.0776	1.0789	1.0811
40	1.0348	1.0379	1.0427
60	0.9943	0.9991	1.0078
80	0.9592	0.9660	0.9771
100	0.9332	0.9393	0.9513
120	0.9139	0.9175	0.9317
140	0.9009	0.9033	0.9210
160	0.8972	0.8954	0.9168
180	0.9007	0.8953	0.9191
200		0.9052	0.9279

There are several ways to determine the deviation of a gas in the regions of pressure below one atmosphere. The first is to expand a known volume of gas into successively larger volumes and to note the pressure changes at constant temperature. This procedure was carried out by Boyer and Morrison (1) on a natural gas of similar composition to the one used in the present experiments. They report a linear variation of PV with P but it was impossible to determine the slope of the graph with sufficient accuracy for the purpose in mind.

A method which gives considerably greater accuracy, is to extrapolate the graph of $(PV)_{25}/(P_1V_1)_{25}$ vs P from 40 atmospheres to 0 atmospheres. In this range, the graph is a straight line and extrapolation is very accurate in regions of low pressure. The value of $(PV)_{25}$ at 60 cm. of mercury is accurately known from density measurements, and from the slope of the graph of $(PV)_{25}/(P_1V_1)_{25}$ through this point, it is possible to get an absolute value of $(P_1V_1)_{25}$. Extrapolation of the line to zero pressure enables one to calculate an absolute value of $(P_0V_0)_{25}$ from which a more accurate calculation of the molecular weight can be made than was possible from the density value at 60 cm. pressure.

In the present instance, it was necessary to assume that the deviation of the gas from ideality in the region of 0 - 1 atmosphere at 25°C was the same as that of the Alberta Oil Incomes #2 gas used by Boyer and Morrison. This gives a deviation per cm. of 0.00003815. This was

used to correct the $(P_1V_1)^1$ values from the measured pressure in the vicinity of 60 cm. and 25°C to 76 cm. and 25°C. This gave the corrected value of $(P_1V_1)_{25}$. From the slope of the plot of $(PV)_{60}/(P_1V_1)_{25}$ vs P in the region 0 - 34 atmospheres the value of $(P_oV_o)_{60}/(P_1V_1)_{25}$ was found to be 1.12047. Since Boyle's and Charles' Laws apply exactly to ideal gases, they can be applied accurately to real gases at zero pressure. Thus a value of $(P_oV_o)_{25}/(P_1V_1)_{25}$ is readily obtained from the value of $(P_oV_o)_{60}/(P_1V_1)_{25}$ by using the factor 298.16/333.16. This yields a value of $(P_oV_o)_{25}/(P_1V_1)_{25}$ of 1.00276 as compared with 1.00290 for Alberta Oil Incomes #2. It was considered more accurate to assume a correction factor for $(P_1V_1)^1$ over a small range of pressure (16 cm. approximately) and from this corrected value to calculate the slope of the $(PV)_{25}/(P_1V_1)_{25}$ vs P curve, than to assume the same slope as existed for Alberta Oil Incomes #2 gas.

It is obvious that the value of $(PV)_{25}/(P_1V_1)_{25}$ at one atmosphere is 1.0000. From this value, and the value calculated for the slope at zero atmospheres, it is possible to calculate the ratio at 60 cm. pressure. Thus $(P_{60}V_{60})_{25}/(P_1V_1)_{25} = 1 + 16/76(0.00276) = 1.00058$. From this ratio and the value of $(P_{60}V_{60})_{25}$ obtained from densities, we get $(P_1V_1)_{25} = 1226.13$ cc. atm./g. Extrapolation of this line to zero pressure, as described above, yields a value of $(P_oV_o)_{25} = 1229.51$ cc.atm./g. This value yields a molecular weight of 19.91 g. for the gas.

The molecular weight of the gas can also be found from its composition as determined by the low temperature fractionation column. The result by this method, is a molecular weight of 20.49 g. This is a considerably larger error than was found by Boyer and Morrison. The discrepancy can tentatively be ascribed to inaccuracy in experimental technique either with the analysis column or in taking densities.

It is now desired to obtain a specific value of PV at 60°C. This can be done in one of three ways.

(1) The variation of pressure with temperature on a constant volume of gas may be used in conjunction with the accepted value of $(PV)_{25}$. This method is not considered accurate enough for the present measurements (1)

(2) The value of $(P_0V_0)_{60}$ may be determined directly from $(P_0V_0)_{25}$ if the latter is known. Since this procedure is used in reverse, to determine $(P_0V_0)_{25}$ from $(P_0V_0)_{60}$ in this work, this method is excluded.

(3) The slope of the line $(PV)/(P_1V_1)_{25}$ vs P can be used in conjunction with the accepted value of $(P_1V_1)_{25}$. By this method, a value of $(P_0V_0)_{60} = 1373.84$ cc.atm./g. was obtained. Considering the errors in density measurement, this value is probably accurate to closer than 1 cc.

The experimental values of $(PV)_{60}/(P_1V_1)_{25}$ vs P are shown in Figure 2. From calculated values of $(P_0V_0)_{25}$ and $(P_0V_0)_{77}$ and, in the case of the 25°curve, from the calculated slope, tentative compressibility curves at 25° and 77° are also presented. Data obtained by Boyer

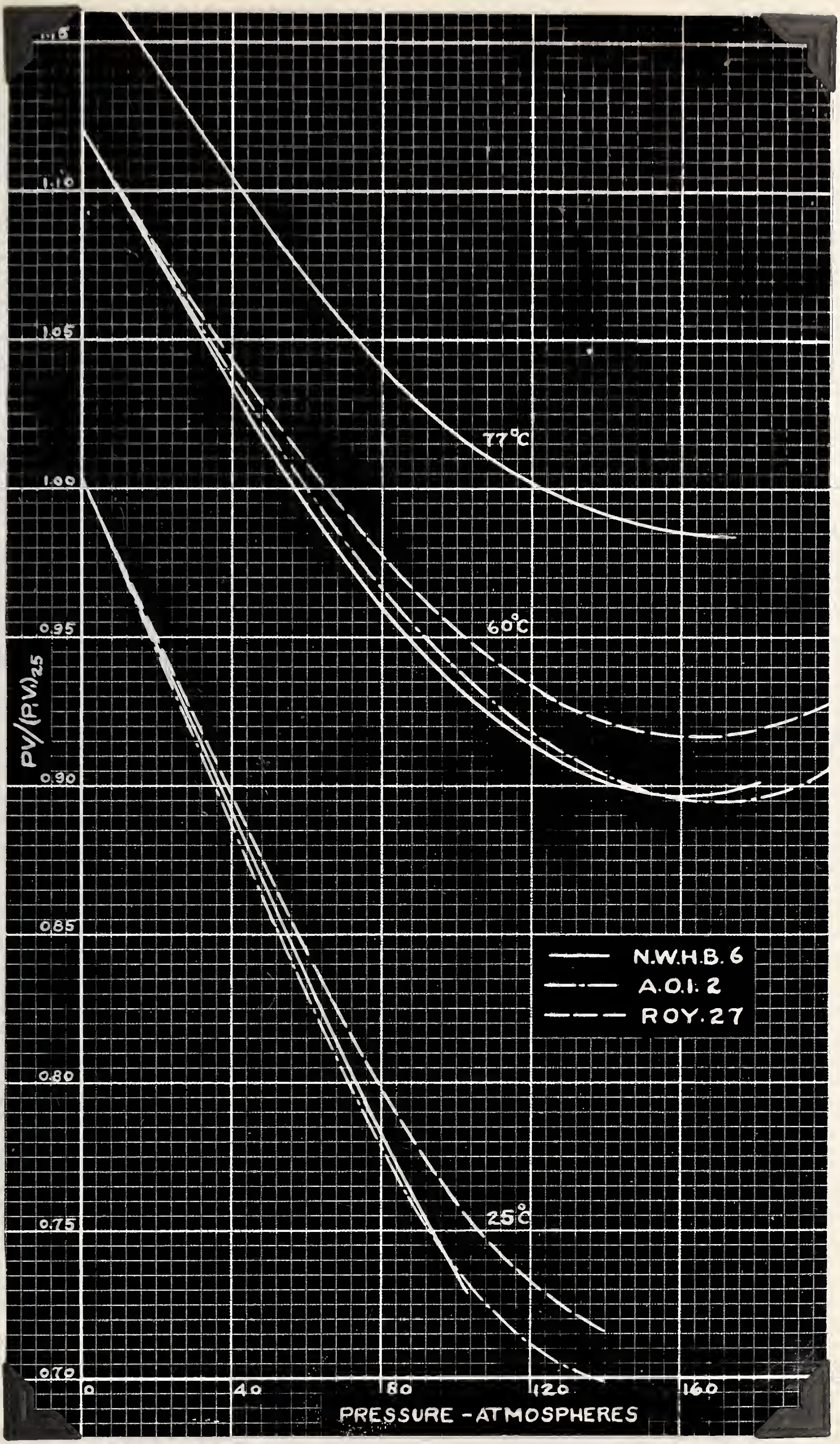

Figure 2

Pressure - Volume - Temperature Relationships.

and Morrison (1) and Gillies and Hugill (6) are presented for comparison.

The general trend of Pv vs P curves can be predicted from an equation of state such as that of Van der Waals:

$$(P + A/V^2)(V - B) = RT.$$

Rearranged, this becomes -

$$PV = RT + PB - A/V + AB/V^2$$

At low pressures, P is small and V is relatively large. Hence the term A/V is considerably more significant than $(PB + AB/V^2)$. Thus, as P increases, the negative value of A/V causes PV to decrease. However, simultaneously PB is increasing and, due to the decrease in V, AB/V^2 is also increasing. Due to the fact that AB/V^2 increases at a faster rate than does A/V, the positive value of $PB + AB/V^2$ soon predominates over the negative value of A/V and the slope of the curve becomes positive. For this gas, this occurs in the region of 150 atmospheres.

By comparison of the compressibility curves for the three gases at 60°C, it will be evident that the ease of compressibility increases from Royalite #27 to Alberta Oil Incomes #2 to N.W. Hudson's Bay #6 in the low pressure region. This may be explained in view of the different compositions of the three gases.

It will be noted that an increase in the content of propane and pentane + occurs from Royalite #27 to Alberta Oil Incomes #2 to N.W. Hudson's Bay #6. Royalite #27 and Alberta Oil Incomes #2 have the same butane content but that of N.W. Hudson's Bay #6 is greater. It is thus

evident that the concentration of higher hydrocarbons increases progressively from Royalite #27 to Alberta Oil Incomes #2 to N.W. Hudson's Bay #6. The average concentration as shown by the molecular weight of the gas shows the same regular trend.

	Molecular weight (from analyses)	Density g/litre
Royalite #27.	19.96	0.8006
Alberta Oil Incomes #2	20.33	0.8278
N.W.Hudson's Bay #6.	20.49	0.8151

The gas densities, shown for comparison, are not quite so regular, but the low temperature fractionation is considered to give a more ideal result.

The trend of the PV vs P curve is, as has been discussed above, the result of two opposing factors:

1. The force of intermolecular attraction tending to decrease the value of PV due to the negative sign of the term A/V.

2. The volume occupied by the molecules tending to increase the value of PV due to the positive sign of the term PB. The relative values of A and B will determine the effect of the term AB/V^2.

In the case of the gases under consideration, it might be expected that the increase in the content of higher hydrocarbons from Royalite #27 to N.W. Hudson's Bay #6 would tend to increase the effect of the -A/V term. In regions of moderately low pressure, where the volume of the molecules is relatively unimportant, the intermolecular attraction between large molecules such as pentane would be expected to be much greater than similar

forces between the smaller methane molecules. Hence, increasing the pentane content of the gas would increase the importance of the term involving intermolecular attraction. Provided the pressure was moderately low, the effect of the larger pentane molecule on the term involving molecular volume would be insignificant. Thus, at low pressures, the reason for the relative positions of the three PV vs P curves is evident.

As pressure increases, the molecular volume term becomes relatively more important, and, as has been seen before, a pressure is reached at which $(PB + AB/V^2)$ increases more rapidly than does A/V and a minimum in the PV curve is reached. In a gas having a higher pentane content, this pressure would be reached sooner, due to the effect of the larger pentane molecules. This is evident in the curves illustrated. The line for N.W. Hudson's Bay #6 reaches a minimum and has started to increase before the minimum is reached in either the Alberta Oil Incomes #2 curve or the Royalite #27 curve.

The effect of decreasing temperature is to increase the relative importance of the molecular attraction term. This is evidenced by the increase in the negative slope of the PV curve in going from 77° to 60° to 25°. The general trend of the three curves at 25° is the same. The position of the curve at 77° for N.W. Hudson's Bay #6 is in agreement with what might be expected from the behavior of Alberta Oil Incomes #2 at 98° as measured by Boyer and Morrison(1)

Reference was made earlier to the deviation per cm. obtained by Boyer and Morrison. This was obtained from the expression -

$$P_0V_0/P_1V_1 = 1 + \lambda = 1 + b\Delta P$$

Where

λ = deviation facter

b = deviation factor per cm.

The value of PV at any pressure and temperature within the experimental range is readily obtained from large scale plots of $(PV)_T/(P_1V_1)_{25}$ vs P. Knowing the slope of the curve at the desired point, it is only necessary to multiply by the accepted value of $(P_1V_1)_{25}$ to get an absolute value of $(PV)_T$. This, in turn, yields a value of V, ie. the specific volume, which may be inverted to give the density.

In addition to this direct use of the PV data, they are of value in formulating equations of state, the coefficients of which lead to interatomic forces and theoretical considerations of the gaseous state. It is also possible, although rather difficult, to calculate thermodynamic properties of gases from the pressure-volume-temperature data. A detailed description of the method involved is given by Newitt (14). This, in most cases, requires a knowledge of V - T coefficients.

Graphs of V vs T yield very inaccurate values of the coefficients and it is highly preferable to use the variation in "residual volume" rather than actual volume. This residual volume has already been discussed in more detail previously. Using the method outlined above, the

residual volumes were calculated for N.W. Hudson's Bay #6 gas at 60°C. The results are shown in Figure 3 and Table 4. For comparison, the figures for Alberta Oil Incomes #2 and Royalite #27 are included.

It will be noticed that in all three cases, "a" is positive at low pressures and follows a general trend to negative values at high pressures. The residual volume, "a", will necessarily be zero when $P_0V_0 = PV$.

The trend of "a", from positive to negative values can likewise be predicted from consideration of a suitable equation of state such as that of Van der Waals:

$$(P + A/V^2)(V - B) = RT.$$

Rearranging, we get $a = RT/P - V = A/PV - AB/PV^2 - B$. When pressure is low, V is large and the term AB/PV^2 can be neglected. Also PV changes only slightly with small changes in pressure. Hence

$$a = A/PV - B = \text{Constant}.$$

Actually PV does change for small changes in pressure, but small variations in A and B, compensate and keep "a" constant. This is readily seen in the graph of a vs P in the region 0 - 40 atmospheres. As pressure is increased, V becomes smaller and the term AB/PV^2 soon predominates over A/PV due to the second power of V. Thus a decrease in "a" can be predicted with increase in pressure and ultimately "a" will become negative.

Changes in "a" with temperature can be predicted roughly by substituting RT for PV in the Van der Waal's expression. Thus

$$a = A/RT - ABP/R^2T^2 - B.$$

Table 4

Residual Volumes, cc/g, at 60°C

P.atm.	N.W.H.B.#6	A.O.I. #2	Royalite 27
1	2.629	2.538	2.449
20	2.629	2.538	2.449
40	2.629	2.511	2.426
60	2.578	2.455	2.344
80	2.472	2.341	2.238
100	2.296	2.195	2.113
120	2.110	2.048	1.964
140	1.923	1.878	1.780
160	1.710	1.703	1.590
180	1.498	1.514	1.397
200		1.303	1.202

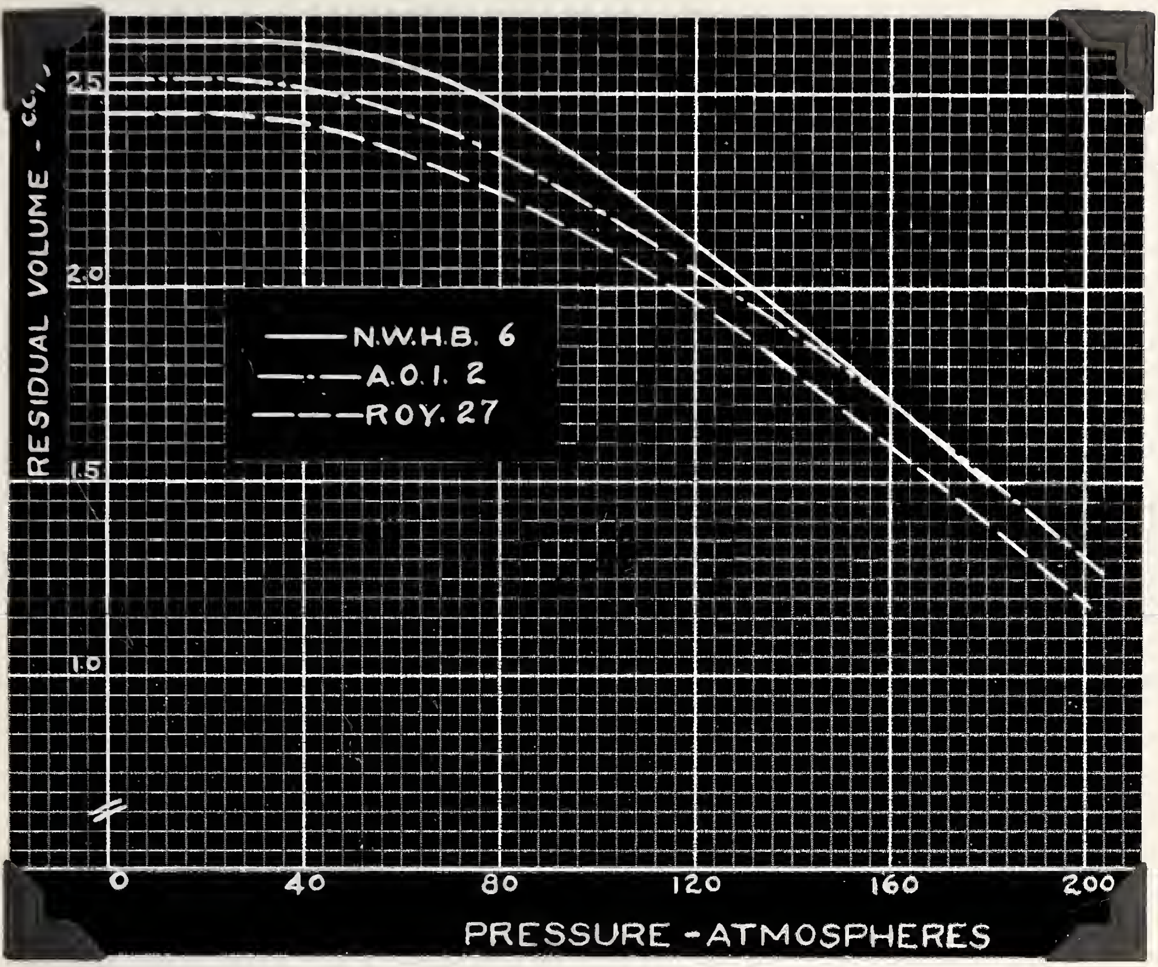

Figure 3

The Variation of the "Residual Volume"
with Pressure.

An increase in temperature will obviously decrease "a" and a point will eventually be reached where "a" is no longer positive for any value of pressure. The point at which a = 0 when P = 0 is called the Boyle Point.

Changes in residual volume with composition can be seen by a similar treatment to that used above for the compressibility curves. In the low pressure region, where changes in B are negligible for increase in the proportion of higher hydrocarbons in the gas, the increasing importance of A in going from Royalite #27 gas to N.W. Hudson's Bay #6 gas will cause the residual volume to increase. This is evidenced by the higher initial value of "a" for the latter gas. As the pressure increases, the larger concentration of higher hydrocarbons in N.W. Hudson's Bay #6 gas causes the effect of molecular volume to be felt at a lower pressure than is the case for the other two gases. Thus it is not surprising that the curve for N.W. Hudson's Bay #6 gas crosses the curve for Alberta Oil Incomes #2 gas at 164 atmospheres. At a still higher pressure it is to be expected that this curve will likewise cross the curve for Royalite #27.

The preceding discussions on the behaviour of the gas as predicted by Van der Waals is not quantitative because of the limited accuracy of the Van der Waals' equation of state. A more exact analysis would necessitate a much more complex equation of state and the difficulties involved have already been pointed out. It has also been

shown that a quantity called fugacity can be employed to render the simple equations exact for a real gas. Reference has also been made to an easy method by which fugacities can be calculated from residual volumes determined from pressure-volume-temperature measurements.

Fugacities calculated for N.W. Hudson's Bay #6 gas are shown in Table 5 and illustrated graphically in Figure 4. Fugacities for Alberta Oil Incomes #2 are shown for comparison, in Table 5.

From the effect of composition on the residual volume, it would be expected that the larger proportion of higher hydrocarbons in the N.W. Hudson's Bay #6 gas would result in a lower measured fugacity at the lower pressures. This is readily seen to be the case. As the pressure increases, the effect of the molecular volume term, B, in the Van der Waals expression becomes apparent and the residual volume for N.W. Hudson's Bay #6 decreases much more rapidly than that for Alberta Oil Incomes #2. A pressure will eventually be reached at which the areas under the two a vs P curves are the same and the measured fugacities at this pressure will be the same for the two gases. With further increase in pressure, the fugacity of N.W. Hudson's Bay #6 gas will exceed that of Alberta Oil Incomes #2 gas.

The absolute differences between the fugacities of the two gases at any pressure within the range studied, is slight as would be expected in view of their close similarity in composition.

Table 5

Fugacities at 60°C

P. atm.	N.W. Hudson's Bay #6.		Alberta Oil Incomes#2	
	f_1	f_2	f_1	f_2
1	0.998			
20	19,25	18.79	19.26	18.86
40	37.05	35.70	37.10	35.87
60	53.51	51.53	53.62	51.74
80	68.77	66.40	68.98	66.60
100	83.03	80.65	83.36	80.79
120	96.48	94.45	96.92	94.56
140	109.30	107.91	109.82	107.96
160	121.65	121.14	122.21	121.14
180	133.70	134.22	134.23	134.18
200			146.04	147.18

f_1 = experimental fugacity values

f_2 = fugacities calculated from fugacities of pure components using Lewis' rule.

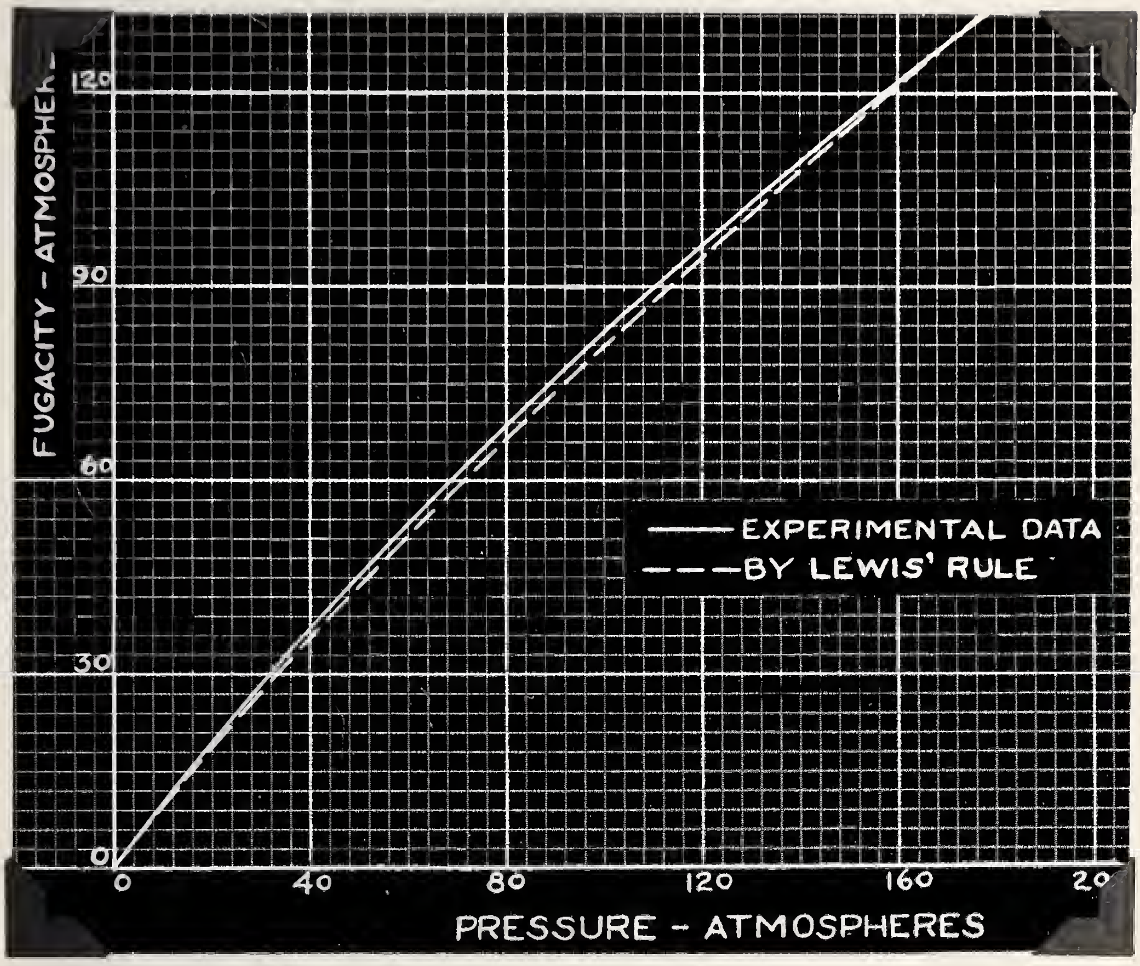

Figure 4

The Variation of Fugacity with Pressure.

The fugacities of the pure components, used in the application of Lewis' rule, are the same as those used by Boyer and Morrison and are, in the main, from the investigations of Sage and Lacey. As shown by Boyer, the application of Lewis' rule in calculation of fugacities of gaseous mixtures is of considerable value, especially in engineering calculations.

Symbols

W_g - Grams of gas as butanes and lighter.

W_p - Total grams in phase.

(V_g)- Volume of gas, butanes and lighter, at t^oC and 1 atm.

(V_o)- Volume of oil, pentanes and heavier, in same units as (V_g).

F_g - Cubic feet of gas, butanes and ligher, at 20°C, 1 atm.

Bbl- 35 Imperial gallons.

W_o - G. of oil, including pentanes and heavier.

V_p - Volume of phase under equilibrium conditions, $(V_p)_g$ for gas phase; $(V_p)_L$ for liquid phase.

G_o - Gallons of oil, pentanes and heavier, at 20°C.

F_p - Volume of phase under equilibrium conditions in cubic feet.

X_p - Volume of phase when expanded to 1 atm. and 25°C.

K_1 - Ratio of grams of methane per cc. of gas phase to grams of methane per cc. of liquid phase.

K_2, K_3, K_4, K_n similar ratios for ethane, propane, butane and nitrogen.

K_c - Ratio of grams of light fraction $(C_5H_{12}+)$ per cc. of gas phase to grams of same fraction (as determined by refractive index) per cc. of liquid phase.

K_{1+n} Ratio of grams of methane + nitrogen per cc. of gas phase to grams of methane + nitrogen per cc. of liquid phase.

Table 6

General Experimental Data

	70°	77°	85°
Liquid Phase Samples:	59.59 cc.	59.61 cc.	59.62 cc.
Gas Phase samples:	27.94 cc.	27.95 cc.	27.97 cc.

Original Materials (as received in the laboratory)

Run No.	1	2	3	5	6	7
Pressure at equilibrium, atm.	228.1	167.5	182.8	205.1	169.7	180.0
Temperature at equilibrium	76.4	77.0	77.0	77.0	70.0	85.0
Oil, cc. at 25°C	692.53	596.52	621.25	656.52	614.44	615.10
Oil, g.	561.71	483.84	503.90	532.51	498.38	498.91
Gas, cc. at 25°C, 1 atm.	151996	137915	145339	153998	141164	139560
Gas, g.	123.89	112.41	118.47	125.52	115.06	113.76
cc gas, 25°C, 1 atm/cc oil, 25°C	219.5	231.2	233.9	234.6	229.7	226.9
Cu. ft. gas, 25°C, 1atm/bbl oil 25°C	1218.9	1283.9	1298.9	1302.7	1275.6	1260.0

Original Materials Charged.

	1	2	3	5	6	7
Oil, cc pentane +, 25°	697.16	600.70	625.69	661.22	618.75	619.38
Oil, g.	564.59	486.45	506.66	535.43	501.06	501.57
Gas, cc butane -, 25°, 1 atm.	151076	137081	144460	153066	140310	138716
Gas, g.	121.01	109.80	115.71	122.60	112.38	111.10
cc. butane - 25°, 1 atm/ cc pentane +, 25°	216.7	228.2	230.9	231.4	226.8	224.0
Cu. ft. butane - /bbl pentane +	1203.4	1267.2	1282.2	1285.0	1259.5	1243.9

Liquid Phase Sample

Liquid Separated	1
g.	30.58
density, g/cc, 20°C	0.8298
volume, cc, 20°C	36.85
molecular weight	178.0
volume, light fraction, cc	4.75
weight, light fraction, g.	3.38
Gas volume, cc, 25°C, 1 atm.	6831.51
Gas density, g/litre, 25°C, 1 atm	0.8625
Gas mass, g.	5.8922

Composition of gas, mole %	
CH_4	75.77
N_2	2.91
C_2H_6	12.22
C_3H_8	6.25
C_4H_{10}	1.89
C_5H_{12}+	0.96

Gas Phase Sample

Liquid Separated	
g.	0.5728
refractive index, 20°C	1.3969
molecular weight	94.5
density, g/cc, 20°C	0.7107
Gas volume, cc, 25°C, 1 atm.	6329.99
Gas density, g/litre, 25°C, 1 atm.	0.7876
Gas mass, g.	4.9855

Composition of gas, mole %	
CH_4	84.71
N_2	3.53
C_2H_6	7.13
C_3H_8	2.50
C_4H_{10}	1.48
C_5H_{12} +	0.65

Liquid Phase Sample

Liquid Separated	1	2	3	5	6	7
g.	30.58	35.90	34.68	34.20	36.92	36.50
density, g/cc, 20°C	0.8298	0.8188	0.8225	0.8205	0.8211	0.8227
volume, cc, 20°C	36.85	43.84	42.16	41.68	44.96	44.37
molecular weight	178.0	187.5	186.1	188.0	175.0	183.2
volume, light fraction, cc	4.75	6.09	6.37	5.08	7.42	4.48
weight, light fraction, g.	3.38	4.14	4.49	3.48	5.21	3.23
Gas volume, cc, 25°C, 1 atm.	6831.51	5320.75	5879.68	6248.48	5552.17	5462.12
Gas density, g/litre, 25°C, 1 atm	0.8625	0.8899	0.9477	0.8884	0.9300	0.9216
Gas mass, g.	5.8922	4.7349	5.5722	5.5511	5.1635	5.0339
Composition of gas, mole %						
CH_4	75.77	74.00	71.11	73.46	71.11	72.08
N_2	2.91	1.66	2.66	3.30	3.12	3.49
C_2H_6	12.22	14.07	13.23	12.42	13.44	13.01
C_3H_8	6.25	6.59	6.84	6.90	7.34	6.87
C_4H_{10}	1.89	2.26	4.23	2.58	3.45	3.08
$C_5H_{12}+$	0.96	1.42	1.93	1.34	1.54	1.47

Gas Phase Sample

Liquid Separated	1	2	3	5	6	7
g.	0.5728	0.3324	0.4956	0.5670	0.3851	0.3202
refractive index, 20°C	1.3969	1.3931	1.3982	1.3936	1.3961	1.3869
molecular weight	94.5	92.1	95.4	92.4	94.0	88.8
density, g/cc, 20°C	0.7107	0.6798	0.7050	0.6856	0.7015	0.7212
Gas volume, cc, 25°C, 1 atm.	6329.99	4713.09	5066.75	5611.01	4826.97	4777.30
Gas density, g/litre, 25°C, 1 atm.	0.7876	0.7669	0.7442	0.7608	0.7399	0.7636
Gas mass, g.	4.9855	3.6145	3.7707	4.2689	3.5715	3.6479
Composition of gas, mole %						
CH_4	84.71	85.16	84.17	85.36	85.86	85.10
N_2	3.53	3.64	4.99	4.04	4.18	4.01
C_2H_6	7.13	6.90	7.18	7.04	6.82	7.14
C_3H_8	2.50	2.40	2.34	2.29	2.14	2.22
C_4H_{10}	1.48	1.11	0.93	0.77	0.64	0.93
$C_5H_{12}+$	0.65	0.79	0.39	0.50	0.36	0.60

Table 7

Properties of Gas and Liquid Phases and of the System at Equilibrium.

Run No.	1	2	3	5	6	7
Pressure, atm.	228.1	167.5	182.8	205.1	169.7	180.0
Temperature.	76.4	77.0	77.0	77.0	70.0	85.0
Liquid Phase						
Volume, cc $(V_p)_L$	1070.8	783.4	833.5	903.6	779.5	791.4
Mass, g.	655.12	534.00	562.78	602.61	550.48	551.29
Density, g/cc.	0.6118	0.6817	0.6752	0.6669	0.7062	0.6966
Composition in Weight %						
CH_4	9.26	6.34	6.86	7.49	6.18	6.28
N_2	0.62	0.25	0.45	0.59	0.47	0.53
C_2H_6	2.80	2.26	2.40	2.38	2.19	2.12
C_3H_8	2.10	1.55	1.82	1.94	1.75	1.64
C_4H_{10}	0.84	0.70	1.48	0.95	1.08	0.97
Light fraction	9.80	10.74	11.99	9.37	12.98	8.35
Residue	74.58	78.16	75.00	77.28	75.35	80.11
W_g/W_p	0.1563	0.1110	0.1300	0.1335	0.1167	0.1155
$(V_g)_{20}/(V_p)_L$	111.60	86.52	95.11	101.68	90.20	88.76
$(V_g)_{20}/(V_o)_{20}$	179.07	116.68	132.78	144.08	118.50	118.25
F_g/bbl, C_5H_{12}+	994.40	647.94	737.35	800.10	658.05	656.66
Gas Phase						
Volume cc, $(V_p)_g$	153.2	440.6	390.5	320.4	444.5	432.6
Mass, g.	30.47	62.22	59.59	55.43	62.94	61.39
Density, g/cc.	0.1989	0.1412	0.1526	0.1730	0.1416	0.1419
Composition in Weight %						
CH_4	63.63	65.75	63.10	64.44	66.95	66.49
N_2	4.63	4.91	6.53	5.32	5.70	5.47
C_2H_6	10.04	9.98	10.08	9.96	9.97	10.46
C_3H_8	5.17	5.09	4.83	4.75	4.58	4.77
C_4H_{10}	4.03	3.10	2.53	2.11	1.80	2.62
Light fraction	12.50	11.17	12.93	13.42	11.00	10.18
$W_o/(V_p)_g$ in cc.	0.0249	0.0158	0.0197	0.0232	0.0156	0.0145
$G_o/(F_p)_g$	0.0057	0.0038	0.0045	0.0054	0.0036	0.0033
G_o/X_p in 1000 cu. ft.	0.0244	0.0220	0.0243	0.0264	0.0203	0.0190
$X_p/(V_p)_g$ in same units.	231.82	171.78	185.83	206.09	176.35	173.95

System Properties

	1	2	3	5	6	7
$(V_p)_g/(V_p)_L$	0.1431	0.5625	0.4685	0.3546	0.5702	0.5466
Equilibrium Constants						
K_1	2.233	2.148	2.075	2.230	2.174	2.158
K_2	1.170	0.916	0.951	1.089	0.916	1.021
K_3	0.798	0.679	0.602	0.636	0.524	0.596
K_4	1.569	0.917	0.390	0.578	0.338	0.544
K_c	0.416	0.216	0.243	0.371	0.170	0.249
K_N	2.421	4.059	3.333	2.359	2.455	2.108
K_{1+N}	2.244	2.220	2.151	2.239	2.194	2.154

5
205.1
77.0

903.6
602.61
0.6669

7.49
0.59
2.38
1.94
0.95
9.37
77.28

0.1335
101.68
144.08
800.10

320.4
55.43
0.1730

64.44
5.32
9.96
4.75
2.11
13.42

0.0232
0.0054
0.0264
206.09

Equilibrium Measurements

The direct experimentally-determined data are presented in Table 6. The derived data are shown in Table 7. In experiments 1, 2, 3 and 5 an attempt was made to approach the reservoir conditions of temperature and gas:oil ratio, while allowing the equilibrium pressure to vary above and below that existing in the reservoir. In experiments 6 and 7 an attempt was made to maintain the reservoir conditions of pressure and gas:oil ratio while allowing temperature to vary above and below that existing in the reservoir. A further series of two experiments was done in which an attempt was made to maintain the reservoir conditions of pressure and temperature while allowing the gas:oil ratio to vary. Unfortunately no results were obtained in this last series due to failure of the high pressure apparatus during the analyses. Temperature control was very exact in all cases but it was much more difficult to introduce the size of charge which would give simultaneously a desired pressure and a desired gas:oil ratio. In all cases except in the first table on "original materials (as received in the laboratory)" the term "gas" refers to butanes and lighter, and "oil" refers to pentanes and heavier constituents.

The weight of liquid separated from the liquid phase was found to ±0.01 g. and its density was determined gravimetrically. The molecular weight of the oil was determined by the cryoscopic method but so much variation was found in the results that it was considered

inadvisable to use the molecular weights so determined. The reason for this variation is still obscure but may be due to traces of water condensing in parts of the freezing point apparatus and thereby changing the temperature gradient by impeding the rate of heat transfer.

The molecular weight of the light fraction from the gas phase sample is considered to be fairly accurate. The reason for this is that the molecular weight was determined for each sample by comparing its refractive index with a refractive index vs molecular weight graph previously prepared. This graph was prepared by measuring molecular weights of different fractions from a series of A.S.T.M. distillations and represents the best straight line through some 15 points in a fairly narrow molecular weight range (Figure 1). However in view of the unreliability of the molecular weights of liquid from the liquid phase it was considered advisable to deal only with weight fractions for each phase, rather than mole fractions.

The weight of the light fraction from the gas phase was accurately determined by weighing the sealed dilatometer and its volume was determined by immersing the dilatometer in water at 20°C and reading the volume directly from calibrations etched on the dilatometer. The corresponding light fraction in the liquid from the liquid phase was determined by fractional distillation of the liquid and plotting % over vs refractive index. The volume having the same refractive index as the dilatometer sample was considered to be light fraction.

All gas volumes were measured in the vicinity of 53-78 cm. of Mercury at room temperature and corrected using the deviation factor for N. W. Hudson's Bay #6 gas.

Since it is not possible to determine mole fractions on the phase samples, the usual equilibrium constants are replaced by constants determined from concentrations. Thus, in this present case,

$$K_1 = \frac{\text{grams methane per cc. of gas phase}}{\text{grams methane per cc. of liquid phase}}.$$

This K is analogous to the constant in Henry's Law and becomes K_N on multiplication by the ratio of molar volumes in the corresponding phases.

Considering the data in Table 7, we see that the solubility of butanes and lighter in pentanes and heavier components, expressed as cubic feet per barrel (Fg/bbl C_5H_{12+}), increases with increasing pressure and the rate of increase is greater at the higher pressures. This is what would be expected from a consideration of solubility work done by other workers.

Considering runs #2, 6 and 3, 7 it is evident that increasing temperature decreases the solubility of butanes and lighter in pentanes and heavier constituents. However the decrease is larger from 77° - 85° than from 70° - 77°. This may be partially explained by consideration of the other variables involved. Three factors simultaneously affect the solubility values. Consider, first, runs #2 and #6. (1) There is a decrease in pressure of about 2.2 atmospheres in going from 70° - 77° which will cause a slight decrease in solubility. (2) The gas:oil ratio

increases slightly. This will have the effect of increasing the volume occupied by the gas phase, and hence, there will be a more complete transfer of the lighter liquid hydrocarbons to the gas phase. This will leave a heavier liquid residue and the butanes and lighter components will have a decreased solubility. (3) The increase in temperature will have two effects: the normal effect of temperature on solubility -- at low pressures, a temperature increase will cause a decrease in solubility; as the pressure increases a region will be found in which the solubility decreases to a minimum and then increases with increasing temperature. The other effect of increasing temperature is due to the increased vapor pressure of the light liquid fractions. Vaporization of these components leaves a heavier liquid residue in which the gaseous components have a decreased solubility.

Consider, now, runs #3 and #7. The decrease in pressure in going from 77° to 85° is 2.8 atmospheres which is, for practical purposes, identical with the pressure effect on solubility in going from 70° to 77°. The gas:oil ratio, however, decreases in going from 77° to 85° so the effect will be to cause an increase in gas solubility. However, in both temperature ranges the effect of such a small change in gas:oil ratio will be very slight. In the higher temperature range (77° to 85°) the increase in vapor pressure of light liquid components with increase in temperature will be somewhat larger than in the lower temperature range. Thus, one might expect a smaller decrease in solubility

between 70° - 77° than between 77° - 85°. A further variable will be the absolute value of the pressure. As observed by Johnson (8), at low pressures the solubility vs temperature curve has only a slight curvature, which becomes much more pronounced at higher pressures. Thus, it may be that the larger decrease in solubility between 77° - 85° than between 70° - 77°, is partially due to the fact that the former values are at a pressure of 180 atmospheres as compared to 167 atmospheres for the latter values.

The closest comparable data for Alberta Oil Incomes #2 are at 158.6 atmospheres and 98°C. It was considered inadvisable to extrapolate the data for N.W. Hudson's Bay #6 over such a wide range of temperature and pressure.

Considering the vaporization of pentanes and heavier constituents into the gas phase, for N.W. Hudson's Bay #6, expressed as gallons of pentanes and heavier per thousand cubic feet of expanded phase (G_o/X_p), it is apparent, from Runs 2, 3 and 5, that an increase in pressure causes an increase in the pentane + content of the gas phase. A clear distinction should be made, at this point, between gallons of pentanes and heavier per cubic foot of phase at equilibrium $(G_o/(F_p)_g)$ and per cubic foot of expanded phase (G_o/X_p). The former value will always show an increase with pressure as predicted by Poynting. This is evident from the values of $(G_o/(F_p)_g)$ in Table 7. However, the latter value (G_o/X_p) will show an increase with pressure only when the transfer of light liquid components to the gas phase occurs at a

faster rate than can be compensated for by the increased concentration of gaseous components in the gas phase due to compression. Thus G_0/X_p will increase with pressure only in the region of retrograde condensation. At all lower pressures G_0/X_p will decrease. The fact that G_0/X_p increases in going from 167.5 atmospheres to 205.1 atmospheres indicates that the region of retrograde condensation is encountered in this pressure range. Run #1 introduces an anomalous result, in showing a decrease in G_0/X_p with still further increase in pressure. Since this experiment was the first one carried out, the only apparent explanation is that the value of G_0/X_p is in error due to inexperience in handling the analytical apparatus.

Considering the temperature effect, it is evident that three factors affect the transfer of pentane and heavier components to the gas phase. In the temperature range 70° - 77° (Runs #6 and 2) there is a slight decrease in pressure which should cause a slight decrease in G_0/X_p; the simultaneous increase in gas:oil ratio should also decrease the pentane content of the gas phase. Although a more complete transfer of light liquid hydrocarbons to the gas phase might be expected to to accompany an increase in gas:oil ratio, the diluting effect of the lighter gaseous components would result in a net decrease in G_0/X_p. Both the pressure effect and the gas:oil ratio effect will have a very slight influence on the system. In opposition to these effects, is the effect due to increase in temperature, which should

produce a decided increase in G_o/X_p due to the increased vapor pressure of the volatile liquid components. The increase in pentane and heavier constituents in the gas phase due to an increase in temperature would be expected to predominate over the contrary effect of pressure decrease and gas:oil ratio increase. This would account for the higher value of G_o/X_p at 77° (Run #2) than at 70° (Run #6).

Comparing Runs 3, 7 in which the temperature rises from 77° to 85°, it is evident that the decrease in pressure will decrease the value of G_o/X_p by an amount very similar to the effect predicted in the Runs at 70° and 77°. The effect here, will be equally small. The simultaneous decrease in gas:oil ratio will have a slight tendency to increase the transfer of pentanes and heavier constituents to the gas phase, as expressed by G_o/X_p. However, here too, the effect of increased temperature in increasing the vapor pressure of the volatile liquid components would be expected to predominate over all other factors, and an increase in G_o/X_p might be predicted. The fact that a very decided decrease is measured, would lead to the conclusion that Run #7 is very much in error.

The reason for this discrepancy is not apparent. Errors in measuring the pentane + fraction of the gas from the gas phase may be as high as 20% but this is only a small portion (about 15-20% by volume) of the "light fraction" most of which is retained and accurately measured in the dilatometer. The error appears to be in Run #7 rather

than in any of the other runs. A possible explanation for the anomalies observed in Run #7 will be suggested later.

Reference might be made, here, to the difficulty encountered by Boyer and Morrison(1) in the appearance in the gas phase sample of a liquid whose presence could not be accounted for. Further investigations showed that this liquid was carried as spray or as liquid through the lines and trapped in the gas phase pipette due to its horizontal position. In this work an improved design of the apparatus has been used, in which the gas phase pipette occupies a vertical position in the oil bath. This has eliminated all liquid phase, as such, from the gas phase sample. The liquid which does separate out in the dry ice-acetone condensers was present in the pipette as a gas.

Gas phase densities show a decided increase with pressure as shown by comparison of Runs 1, 2, 3 and 5, and Figure 5. This is a result of three factors: (1) normal increase in density due to compression of the gas with increased pressure (2) preferential solubility of propane and butane in the liquid phase from the gas phase (3) transfer of pentanes and heavier components from the liquid phase to the gas phase. The second of these factors tends to decrease the gas phase density in opposition to the combined effects of the other two factors tending to increase the gas phase density. The first and third factors predominate. The net result is an increase in gas phase density which is roughly proportional to the

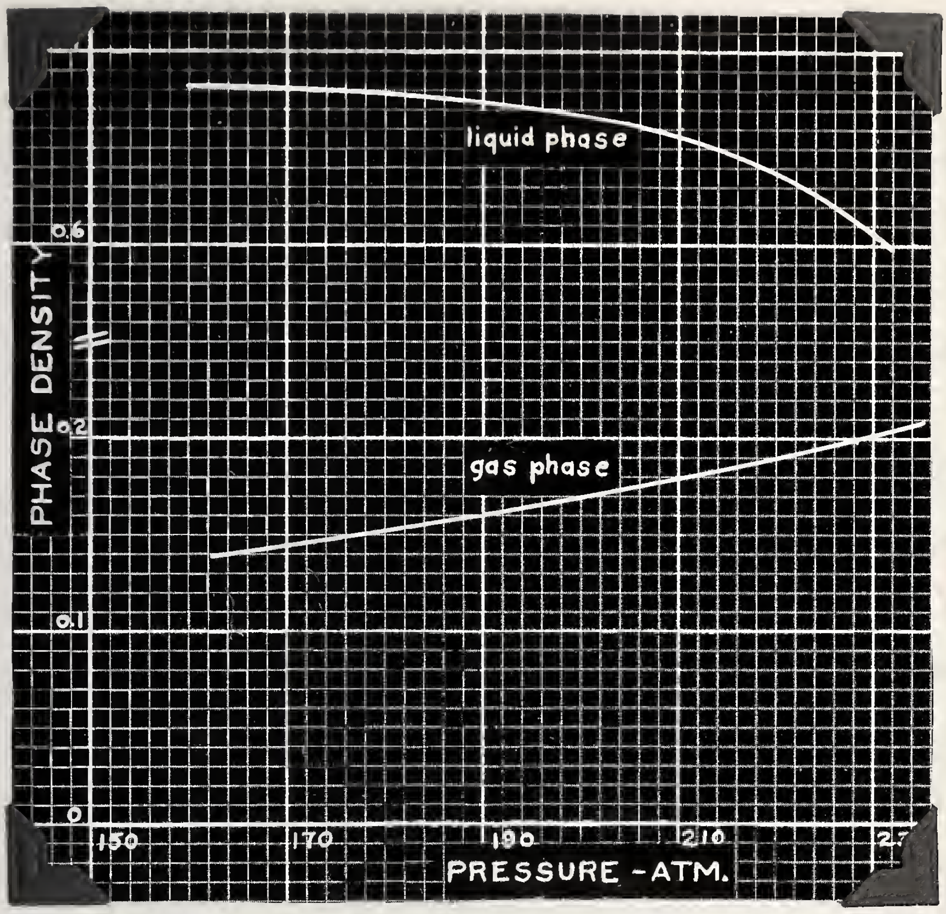

Figure 5.

Variation of Phase Density with Pressure

increase in pressure. The more rapid rate of increase in gas phase density at the higher pressure may be due to the increased rate of transfer of pentane and heavier constituents from the liquid phase.

A simultaneous increase in gas:oil ratio might be expected to decrease the gas phase density due to the diluting effect of the gaseous hydrocarbons on the volatile liquid components. It is difficult to confirm this suspected trend from the data, due to the small variation in gas:oil ratio encountered. The effect is too slight in these experiments to have any significance.

The temperature effect on gas phase density is shown in Runs 2, 6 and 3, 7. There is a two-fold effect of temperature on gas phase density: (1) at constant pressure, an increase in temperature would cause a decrease in density which is roughly proportional to the change in the absolute temperature. This is a direct conclusion from Charles' law. (2) due to the increased vapor pressure of light liquid hydrocarbons, an increased temperature should increase the gas phase density. If the phase density at 77° and 167.5 atmospheres (Run 2) is calculated from that at 70° and 169.7 atmospheres (Run 6) assuming a linear relationship between density and pressure and correcting for temperature on the basis of the change in the absolute temperature, a density of 0.1370 g/cc is calculated for Run #2. The measured value is 0.1412 g/cc. This difference must be a result of the increased vapor pressure of the volatile liquid hydrocarbons at the higher temperature, tending to increase

the gas phase density.

Similar calculation of the gas phase density in Run #7 from that in Run #3 yields a value of 0.1469 g/cc. The measured value is 0.1419 g/cc. It is reasonable to expect that the calculated phase density at 85°C would be lower than the measured value since the calculation does not take into account the increased transfer of light liquid fractions to the gas phase at the higher temperature. The reverse is actually the case here. In view of the anomalies apparent in Run #7 it seems reasonable to assume that the data for Run #7 are in error.

The simple assumption that a state of equilibrium had not been attained at the time of taking samples, serves to explain all the discrepancies which have been observed. The decrease in solubility of gas in oil, as expressed by F_g/bbl $C_5H_{12}+$, for the temperature interval 70^o - 77^o is roughly 10 cu. ft./bbl as compared with 80 cu. ft./bbl decrease for the temperature interval 77^o-85^o. This difference is easily explained if the oil in Run #7 had not become saturated with gas. Similarly, in the transfer of volatile liquid fractions to the gas phase with increasing temperature, a decrease in G_o/X_p is observed between 77^o - 85^o whereas an increase had been predicted on the basis of the behavior of the systems at 70^o and 77^o. If equilibrium had not been attained in Run #7, the transfer of volatile liquid fractions to the gas phase would not be complete, and the value of G_o/X_p would be lower than would be expected.

This incomplete transfer of pentane and heavier components to the gas phase at 85°C due to non-attainment of equilibrium, would also explain why the gas phase density at 85°C calculated from that at 77°C, is higher than the experimental density. If equilibrium had been attained, it is reasonable to assume that the measured density would have been much higher than was actually the case.

The anomalies in liquid phase density to be discussed presently, are also readily accounted for by the assumption that equilibrium had not been attained in Run #7.

It is possible to compare Run #2 with the values obtained for Alberta Oil Incomes #2 at 98°C and 158.6 atmospheres. The measured density for the gas phase for Alberta Oil Incomes #2 was 0.1286 g/cc. Correcting this to 77° and 167.5 atmospheres (as above) gives a value of 0.1440 g/cc. The gas phase density of N.W. Hudson's Bay #6 at the same pressure and temperature is 0.1412 g/cc. The weight of pentane and heavier components per cc. of gas phase is 0.0158 g in N.W. Hudson's Bay #6 as compared with 0.0207 g in Alberta Oil Incomes #2. The higher value in the latter case can be attributed chiefly to the much higher temperature and the resultant increase in vapor pressure of the volatile liquid components. On the basis of the weight of pentane and heavier components in the gas phase, it might be expected that the gas phase density of Alberta Oil Incomes #2 would be greater than that of N.W. Hudson's Bay #6 by

0.0049 g/cc. ie. a gas phase density of 0.1461 g/cc might be predicted for Alberta Oil Incomes #2. This is comparatively close to the value of 0.1440 g/cc quoted above. No account has been taken of the different gas:oil ratios in comparing the two gas phase densities. The lower gas:oil ratio in the Alberta Oil Incomes #2 sample would be expected to increase the gas phase density but no attempt has been made to predict this effect on a quantitative basis.

Consideration of liquid phase densities shows that increased pressure should cause a decrease in the density because of increased solubility of gaseous components at the higher pressures. The increased transfer of volatile liquids from the liquid phase to the gas phase with increasing pressure operates in the reverse manner - i.e. to decrease the liquid phase density. This latter effect is of minor importance compared to the influence of increasing solubility of gas. The decrease in liquid phase density with increasing pressure is clearly shown in Runs 1, 2, 3 and 5, and Figure 5.

An increase in the gas:oil ratio should cause an increased liquid phase density due to more complete transfer of light liquid fractions to the gas phase. This, in itself, should increase the liquid phase density, and in addition there is a decreased solubility of butane and lighter constituents in the heavier liquid residue which is left after transfer of the light liquids to the gas phase. This also would increase the density.

Assuming that the approximately linear relationship between liquid phase density and pressure in Runs 2, 3 and 5 continues to the pressure of Run 1, a liquid phase density of 0.6577 g/cc. can be calculated for Run 1. The difference between this value and the measured value of 0.6118 can be partially ascribed to the decreased gas:oil ratio between Runs 5 and 1.

The effect of temperature on liquid phase density is two-fold: (1) increased temperature will decrease the density due to normal expansion of the liquid (2) increased temperature will increase the density due to increased evaporation of light liquid fractions into the gas phase and simultaneous decreasing solubility of gas in the liquid.

In Runs 2, 6 there is a small decrease in pressure and a small increase in gas:oil ratio, both of which will tend to increase the liquid phase density. The total effect will be very small. The increase in temperature will have a two-fold effect. The measured change is a decrease in liquid phase density which indicates that the decrease in density due to expansion with increasing temperature is greater than the combined effects of the other three factors.

In Runs 3, 7 there is a slight decrease in pressure going from 77° to 85° which should increase the density; simultaneously, the small decrease in gas:oil ratio should decrease the density. Both effects will be small. The two opposing effects of temperature will likewise be felt. The measured change in liquid phase density is an increase. In view of the anomalies previously discussed

in Run #7, it seems reasonable to assume, that, had a state of equilibrium been attained, the liquid phase density would have changed in a manner analogous to the change observed in the temperature interval 70° - 77°.

As explained previously, it was found necessary to express equilibrium constants in terms of concentration ratios rather than mole fraction ratios. On this basis, if the system behaved ideally, Henry's Law predicts a constant K for methane and for methane + nitrogen. The deviation from ideality which might be expected, is a decrease in K for methane with increasing pressure due to the more rapid increase in solubility of methane at the higher pressures. The actual K's for methane are roughly constant for Runs 1, 2 and 5. Run 3 is at variance with the others but no explanation is suggested. The K's for methane + nitrogen are even more constant except for Run 3 which is out of line. It would seem that Henry's Law does apply to methane and methane + nitrogen in this system, with reasonable accuracy, within the pressure range investigated. If the total weight of methane from both liquid and gas phase samples is divided by the total volume of the two phase samples, a value is obtained which represents the approximate concentration of methane at the critical pressure. This value is considerably lower than the concentration of methane in the gas phase and higher than the concentration of methane in the liquid phase for all pressures investigated. It is thus reasonable to predict that K for methane should show a decrease with increasing pressure until it reaches a value

of 1 at the critical pressure where the system is single phase.

K for ethane shows a continued increase with pressure for all pressures investigated. Here, again, Run #3 is out of line with the rest. A calculation of the concentration of ethane at the critical pressure shows that the concentration of ethane should increase in the gas phase and decrease in the liquid phase with increasing pressure. Ideally, K for ethane should decrease from a large value at low pressures to a value of 1 at the critical pressure. In the complex system, K for ethane, having apparently decreased to a minimum, is now increasing with pressure and has exceeded the value of 1 at 200 atmospheres. It might be predicted that a maximum value of K will be attained with increasing pressure, and, at the critical pressure, if it could be attained, K will have decreased again to a value of 1.

Propane and butane both show an initial decrease in K with pressure, followed by an increase. This indicates an increased transfer of these components to the gas phase at the higher pressures. This confirms the statement made previously, that the region of retrograde condensation is encountered in the pressure range investigated.

The general trend of K for the "light fraction" (pentane +) is to increase with pressure, but the inaccuracies in measuring this fraction are so great that very little significance can be placed on the actual numerical results.

K for methane + nitrogen shows very little change with

temperature. All other K's show a tendency to increase with increasing temperature. This can be attributed, in the case of ethane, to the decreased solubility of ethane in the liquid phase at higher temperatures. The change in K is slight. For higher hydrocarbons, the increase in K is due to increased vaporization of these components into the gas phase at the higher temperatures. The effect is very pronounced in the case of butane.

The practical value of these derived data in their application to the Turner Valley field will now be discussed. From the data, it appears that the solubility of butane and lighter in pentane and heavier components at 77°C and 182.8 atmospheres is 737.35 cu. ft/bbl. The actual gas:oil ratio of the well operating at 77°C and 175.4 atmospheres is approximately 1300 cu. ft/bbl. This indicates that N.W. Hudson's Bay #6 well was producing, at the time of sampling, from both a liquid and a gas phase. This is in direct contrast to Alberta Oil Incomes #2 which was considered to be producing from a single liquid phase.

The values listed under G_o/X_p give an indication of the pentane + content of the gas. This will give the well operator the necessary information as to whether his gas is worth scrubbing to recover these volatile fractions.

Other figures in Table 7 are of value in applying the so-called "Brown plan" of operating wells in Turner Valley (2). This plan calls for the removal of a maximum of 25 bbls. of reservoir volume per acre, per well, per day. From a knowledge of the solubility of gas

in oil in the reservoir (F_g/bbl C_5H_{12+}), the gas produced by the well can be divided into two portions: (1) gas originally in solution in the oil in the reservoir, (2) gas originally present as gas phase in the reservoir. From the liquid phase density at equilibrium, one can compute the volume of liquid in the reservoir corresponding to 1 bbl. of oil produced at the surface. From the compressibility of the gas phase, ($X_p/(V_p)_g$), one can compute the volume in the reservoir corresponding to 1000 cu. ft. of gas produced at the surface. With this information at hand, the operator needs only to calculate the total reservoir volume corresponding to one barrel of oil at the surface, at a given gas:oil ratio and from this figure he can readily compute his daily allowable production.

In view of the lack of calculated data on Alberta Oil Incomes #2, it was considered inadvisable to attempt a correlation of results with those obtained for N.W. Hudson's Bay #6. Such comparisons as have been made, indicate a very close similarity in the phase behavior of the two wells. Since the two wells are separated geographically by almost the entire length of the producing horizon, it is apparently not an unjustifiable assumption, to allot production to all wells on the same basis. If the gas solubility in one well had been found to be considerably greater than in the other, then the production of the well with the greater solubility might reasonably have been based on a larger reservoir volume. The fixed allowable reservoir volume set by the "Brown

plan" seems to be justified within the limits of engineering accuracy.

SUMMARY

The pressure-volume-temperature relationships of N.W. Hudson's Bay #6 natural gas have been studied quantitatively at 60°C and qualitatively at 25°C and 77°C over the pressure range 0 - 2750 psi. and comparison made with similar data for Royalite #27 gas and Alberta Oil Incomes #2 gas. Residual volumes and fugacities have also been calculated and comparison made with the same two gases. Fugacities for N.W. Hudson's Bay #6 gas were also compared with those calculated by Lewis' fugacity rule.

Phase equilibrium studies in hydrocarbon systems have been continued and the results of six equilibrium determinations have been presented. The measured and derived data from these determinations have been used to explain the behavior of the complex hydrocarbon systems studied, and the application of the results to the operation of Turner Valley has been indicated.

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